

INFRARED AND RAMAN SPECTRA OF INTRACTABLE CARBONACEOUS
SUBSTANCES--REASSIGNMENTS IN COAL SPECTRA

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INTRODUCTION

Infrared and Raman investigations of intractable carbonaceous materials such as carbon blacks, coal chars, activated carbons, and graphite, have not been possible in the past. Friedel and Hofer have succeeded in obtaining an infrared transmission spectrum of one of the most difficult of these, a coal-based activated carbon (Fig. 1),^{1/} by the use of appropriate sample preparation and instrumental techniques. Extensive and efficient grinding were found to be important. There are other carbonaceous materials, both more and less tractable than activated carbon; the literature contains infrared spectra of formidable materials such as pyrolytic chars,^{2,3,4,5/} carbon blacks,^{6,7/} and coal chars.^{2,8,9/} Coals should also be mentioned here though they are easier to work with; it is possible to obtain good transmission spectra of coals with absorption intensities up to 80 percent.^{5,9,10,11/} The attenuated total reflectance method (ATR) is also suitable for obtaining infrared spectra of coals; J. S. Mattson in recent unpublished work has obtained a spectrum of Pittsburgh coal by the ATR method (private communication). Also, Mattson et al. have published spectra of sorbates on activated carbon using the ATR method.^{12,13/}

Raman spectra of carbonaceous materials have been very difficult to obtain because of the lack, until recently, of appropriate laser light sources. Tuinstra and Koenig have now reported Raman spectra of graphite and various carbons.^{14/} We have obtained Raman spectra of coals and other carbonaceous materials that are reported in this article. In nearly all spectroscopic studies of organic or inorganic materials it is desirable to obtain laser-Raman spectra along with infrared spectra. The two methods are completely complementary and can provide considerable structural information when used together.

Infrared transmission measurements on KBr pellets of various carbonaceous materials have produced good spectra. Accordingly attempts were made to obtain spectra of the most difficult carbonaceous substance--graphite. The infrared absorption of graphite was first studied by Cannon^{15/} who investigated a thin mineral oil mull of graphite. No spectral bands were observed; absorption was essentially the same throughout the 5,000-650 cm^{-1} infrared range. No spectral information was obtainable from such data.

Another unsuccessful attempt was made to obtain absorption spectra of graphite in the infrared (Friedel, unpublished work). Samples were prepared by rubbing powdered graphite on soft polyethylene which retained the graphite as a film; no specific infrared absorption was found. However, absorption and reflectance bands were found in the ultraviolet region with films of graphite on soft polyethylene.^{16/}

Infrared studies of polycrystalline graphite have been carried out by Foster and Howarth who determined spectra of refractive and absorption indices from 1 to 10 microns by a reflection method.¹⁷ One weak absorption peak was observed at $\sim 1300 \text{ cm}^{-1}$, superimposed on a broad band extending from 1 to 10 microns. Coals were also investigated; the spectra obtained were diffuse and not as informative as the conventional absorption spectra of coals.

EXPERIMENTAL

For the present investigation of absorption spectra of carbon black, activated carbons and ground graphite in the $4,000\text{--}250 \text{ cm}^{-1}$ infrared, we applied the sample preparation technique that was successful with activated carbons, namely, very extensive and efficient grinding.¹ Partial spectra were obtained after grinding for 24 hours but for better development of the spectrum many more hours of grinding were required. As noted elsewhere it was necessary to utilize a very small sample, as a large sample softens the blow of the ball bearings used for grinding in a small steel capsule.¹ It is obvious that much more extensive grinding would be required for graphite because of its good lubricating characteristics. Grinding for 96 hours developed a reasonably good infrared spectrum (Fig. 2). The advantageous effect of grinding is illustrated in Figure 3 by the improvement in resolution.

The difficulty of grinding carbonaceous materials increases in this order: Coals, low-temperature chars, carbon blacks (Fig. 4), activated carbons (Fig. 4), carborundum, and graphite. Spectral resolution in all cases improved with grinding; without extensive grinding, scattering difficulties were formidable and only poor resolution conditions could be used.

Perkin-Elmer instruments, PE-21 and PE-521 were used to obtain infrared spectra. Transmission spectra of KBr pellets of the carbonaceous materials were recorded.

Laser-Raman spectra were obtained on a Cary 81 instrument. Coal spectra were obtained on both powders and highly polished solid pieces; analyses of the coals are given in Table 1. Powdered samples of carbon blacks and activated carbons were studied. Graphite was studied both in the form of a ground powder and as a solid piece of Union Carbide highly oriented pyrolytic graphite. A list of materials studied is given in Table 1.

Lasers used: (1) Spectra-Physics, 141 Argon-ion; power delivered to the sample is 40 milliwatts. (2) Spectra-Physics, 125 He-Ne; power delivered to the sample is 35 milliwatts.

DISCUSSION OF RESULTS

1. Graphite and Carbons

The extensive grinding applied to graphite reduces the sample to minute particle sizes on which useful infrared transmission measurements were obtainable. The process works also for various carbon blacks, activated carbons, and carborundum. The frequencies found for ground graphite are essentially the same as those found for the various carbons. By the criterion of X-ray diffraction patterns, it is apparent that the materials measured are not crystalline graphites. Under extensive grinding graphite loses the characteristic X-ray diffraction peaks¹⁸. Nevertheless the infrared spectra obtained on ground graphite provide information concerning the molecular structures involved. Although graphite is altered by the grinding, the disappearance of crystallinity does not mean that the carbon-carbon bondings in the original graphite are altered. The grinding operation does not introduce sufficient energy into the system to break signifi-

cant numbers of carbon-carbon bonds nor to produce reactions that would change the graphitic structure. Therefore it is considered that the infrared spectrum of graphite after extensive grinding is indeed characteristic of the unsaturated molecular structure of graphite (Fig. 2). Two broad infrared bands were observed at 1565 and 1382 cm^{-1} after 72 hours of grinding. With continued grinding to 120 hours the two bands become stronger and sharper, as shown in Figure 3, and the frequencies shift slightly to 1587 and 1362 cm^{-1} (Table 2). In addition to these two absorption bands of graphite there is a weak absorption band at 830 cm^{-1} and another, possibly a combination band, at 2200 cm^{-1} .

These infrared frequencies are very similar to our laser-Raman results and to those reported by Tuinstra and Koenig.^{14/} The results indicate for ground graphite one intense scattering band at 1575 cm^{-1} and a weaker band at 1355 cm^{-1} . Tuinstra and Koenig assigned these frequencies to the E_{2g} and the A_{1g} modes respectively of crystalline graphite with D_{6h} crystal symmetry. The two infrared bands that we find at 1587 and 1362 cm^{-1} compare reasonably well with the Raman bands. Further, the infrared maximum of the strongest band shifts from 1565 to 1587 as particle sizes decrease with grinding. Tuinstra and Koenig found that a closely similar shift occurred in the Raman spectra with decreasing particle sizes. The infrared bands were obtained on ground graphite for which X-ray measurements indicate that the typical fine structure of crystalline graphite has disappeared. And yet, the frequencies observed are practically the same as those of the Raman bands. It appears that the observed infrared and Raman spectra are not related to the crystallinity of graphite. Perhaps vibrations of the "aromatic" structure of graphite, crystalline or non-crystalline, are responsible for the observed spectra.

The weak infrared bands found at 830 and 2200 cm^{-1} are not reported for the Raman spectra. It is likely that the 2200 band is a combination band resulting from the 830 and the 1362 cm^{-1} bands which total 2212 cm^{-1} . This value is reasonably close to the observed 2200 cm^{-1} . The 830 cm^{-1} band could be due to an aromatic impurity in graphite. However, this would then remove the possibility of assigning the 2200 cm^{-1} band as a combination. The Raman spectrum of ground graphite may have a line at 830 cm^{-1} , corresponding to the infrared absorption at 830 cm^{-1} ; there is interfering absorption at 800 cm^{-1} due to a glass prism used in the Raman optical system of the Cary 81 instrument at Carnegie-Mellon University.

2. New Assignments in Coal Spectra

The application of infrared and Raman spectra to the study of intractable carbonaceous material has produced information valuable to researchers involved in studies of the structure of coal. Spectral frequencies are principally assignable to functional groups but some of the important spectral features, not assignable to functional groups, have been involved in considerable conjecture concerning proper assignments. There has been much disagreement in the case of the 1600 cm^{-1} infrared band, the most intense band in coal spectra. After the initial work of Cannon and Sutherland^{10/} the 1600 cm^{-1} infrared band was usually assigned to aromatic structures, thought to be mainly 1-, 2-, and 3-ring compounds. Brown^{8/} and Friedel^{9/} independently proposed that the band is assignable to conjugated, chelated carbonyl structures; derivatives of acetylacetone are known to have very strong and broad bands near 1600 cm^{-1} .^{19/} Friedel and Durie, and their coworkers, ^{20,21/} and Fujii, et al.,^{22/} have made further studies of the 1600 cm^{-1} band using chemical methods along with infrared to substantiate the conjugated chelated C=O structure. Oxygen-18 labeled chars were studied in an unsuccessful effort to prove that oxygen atoms were part of the structure involved in the 1600 cm^{-1} band.^{20,21/}

Table 1.- Coal analyses; graphites and carbons

<u>Coals</u>	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>S</u> (wt.percents)
Lignite (see Table 3)	74.2	4.5	19.4	1.3	0.6
Subbituminous	78.7	5.5	13.3	1.6	0.9
hVBb	80.5	5.5	8.7	1.9	3.4
hVAb (Ohio)	82.4	5.4	8.5	1.3	2.4
hVAb (Pennsylvania)	83.1	5.6	8.7	1.3	1.3
lvb	90.0	4.5	3.4	1.5	0.6
Anthracite	94.2	2.7	1.7	0.8	0.6

Graphite and carbon samples investigated

Pyrolytic graphite, highly oriented piece (Union Carbide & Carbon)

Graphite powder (Ultra Carbon)

Activated carbon, coal-base (CAL Carbon)

Activated carbon, cocoanut-base (UCC carbon)

Carbon black from coal (Bureau of Mines)

Channel black (Micronex)

Table 2.- Infrared and Raman frequencies of graphite (in cm^{-1})

Raman	1582	1360		
Infrared	1587	1362	830 (w)	2200 (w)

Aromatics and/or chelated carbonyls have seemed for some time to be the most likely possibilities to produce the 1600 cm^{-1} band. However, all possible structures have not been investigated. Structures that were seldom considered are included in the group of intractable carbonaceous materials--graphite, carbons, and activated carbons. The infrared and Raman spectra of these have not been available until recently. For coals, in addition to infrared results, the authors have obtained Raman results on seven coals that show two broad lines in each sample in the $1575\text{--}1620$ and $1350\text{--}1400\text{ cm}^{-1}$ regions. Other weak lines have also been found (Table 3).

The Raman spectra of carbons and graphite obtained by Tuinstra and Koenig^{14/} have the characteristic Raman lines at $1575\text{--}1590$ and 1355 cm^{-1} ; they also found that a single crystal of graphite gave only one Raman line at $1575\text{--}1590\text{ cm}^{-1}$. The present authors have found a single Raman line at 1582 cm^{-1} for a highly oriented pyrolytic graphite. We have succeeded in obtaining good infrared spectra for graphite and carbons; practically the same frequencies appear in both infrared and Raman spectra.

It has long been necessary to find an assignment for spectral absorption that exists in the important CH bending region, $1540\text{--}1370\text{ cm}^{-1}$; it has been known since 1959 that completely deuterated chars still show broad relatively intense absorption in this region, even though CH groups are not present.^{23/} Spectra of graphitic structures have their frequencies in the proper region and may be the proper explanation for this unknown absorption. Intensities are important factors in the assignment of infrared bands and Raman lines. The intensity of the infrared band at 1600 cm^{-1} in the spectrum of ground graphite is high, even with the low resolution required for making the measurements. Actually the maximum absorbance of the $\sim 1600\text{ cm}^{-1}$ band is about the same as the 1600 cm^{-1} band in coals. Area intensity is very great, so there is plenty of absorption intensity in the region of the 1600 cm^{-1} band to justify assignment to graphitic structures.

Raman spectra have been run on a variety of coals, both powders and highly polished pieces. It seems reasonable to expect that the Raman and infrared spectra of complex materials like coals should have about the same number of spectral frequencies. We observe nearly 20 bands and band shoulders in infrared spectra but only two broad lines in Raman spectra of coals. Perhaps the small number of Raman lines is due to laser degradation of the samples by the beam. We are not yet certain how drastically combustible materials such as coals are affected by the intense irradiation from a laser beam. We find no evidence of combustion of the coal; no tar or smoke is produced. However, degradation of the samples does occur, as indicated by a spot that appears on the polished surface of each coal specimen as a result of the irradiation. The Raman spectra we observe might be spectra of carbonized coal rather than of coal.

The bands at about 1600 cm^{-1} in infrared and Raman spectra of graphite, carbons and coals are not surprising. The 1600 cm^{-1} band has been known from infrared spectra of coals for a long time. However, the 1360 cm^{-1} band appears to be anomalous at first glance. There is no corresponding band in the infrared spectrum of coals. The peak of the band is at 1360 , but the overall width of the band is very great--much greater than the width of the 1600 cm^{-1} band. In fact the combination of the 1600 and 1360 bands extends from 1800 to 900 cm^{-1} . Figure 5 demonstrates the close comparison of absorption band intensity and band shape in the spectra of coal and ground graphite. The frequency range covered by the two combined bands, 1600 and 1360 cm^{-1} , is almost identically the same as the range found in coal spectra, namely $1800\text{--}900\text{ cm}^{-1}$. Also the low-frequency branch of the band tails off gradually from 1360 to 900 cm^{-1} ; the high-frequency portion of this broad band system drops off precipitously from 1800 to 1600 cm^{-1} . Identically the same thing is observed in coal spectra, with the exception that superimposed

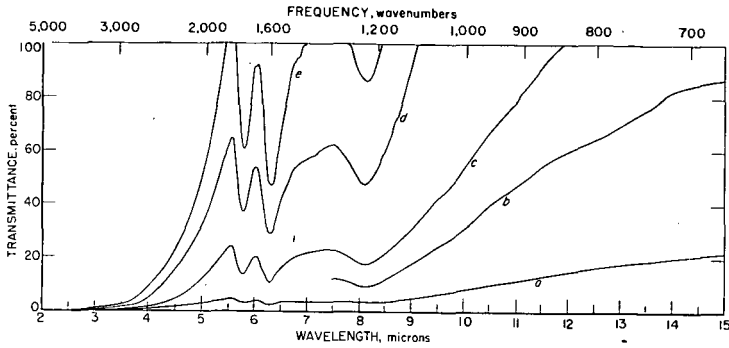


Figure 1

L-11089

Figure 1.- Infrared spectra of Pittsburgh activated carbon, type CAL. Spectrum a: KBr pellet, 0.5 wt % carbon in 200 mg of KBr; spectra b, c, d, e: scale expansions of spectrum a, at 3X, 5.5X, 14X, and 21X, respectively.

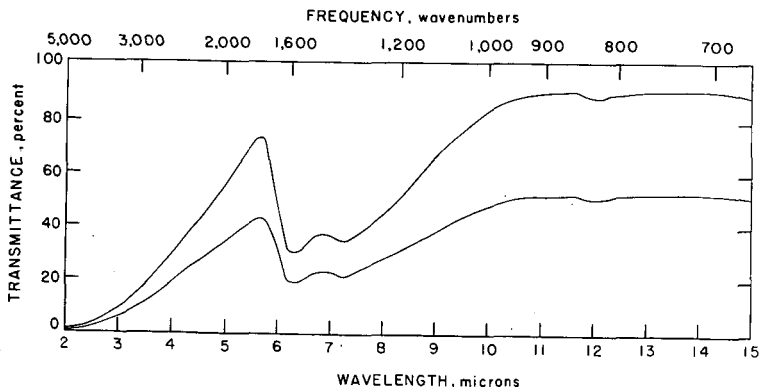


Figure 2

L-11856

Figure 2.- Infrared spectra of graphite after grinding for 96 hours. Bottom curve, as is; top curve is scale-expanded.

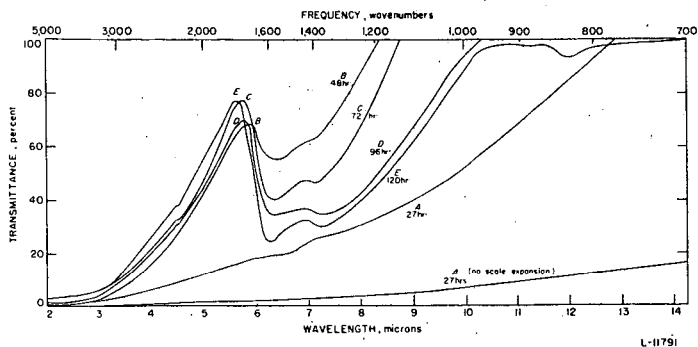


Figure 3

Figure 3.- Infrared spectral intensities of ground graphite increase with efficient grinding. Aliquots were removed from the sample after grinding for the times indicated. Spectra B, C, D, and E are scale-expanded.

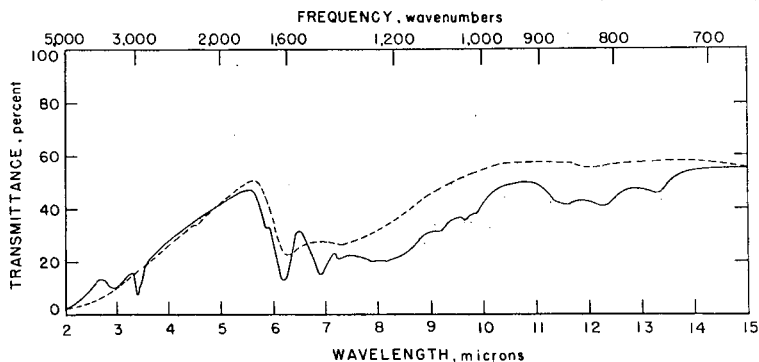


Figure 5

L-11860

Figure 5.- Infrared spectra indicate the close similarity of the intense absorption regions from 1800 to 900 cm^{-1} for Pittsburgh coal —, and ground graphite - - -.

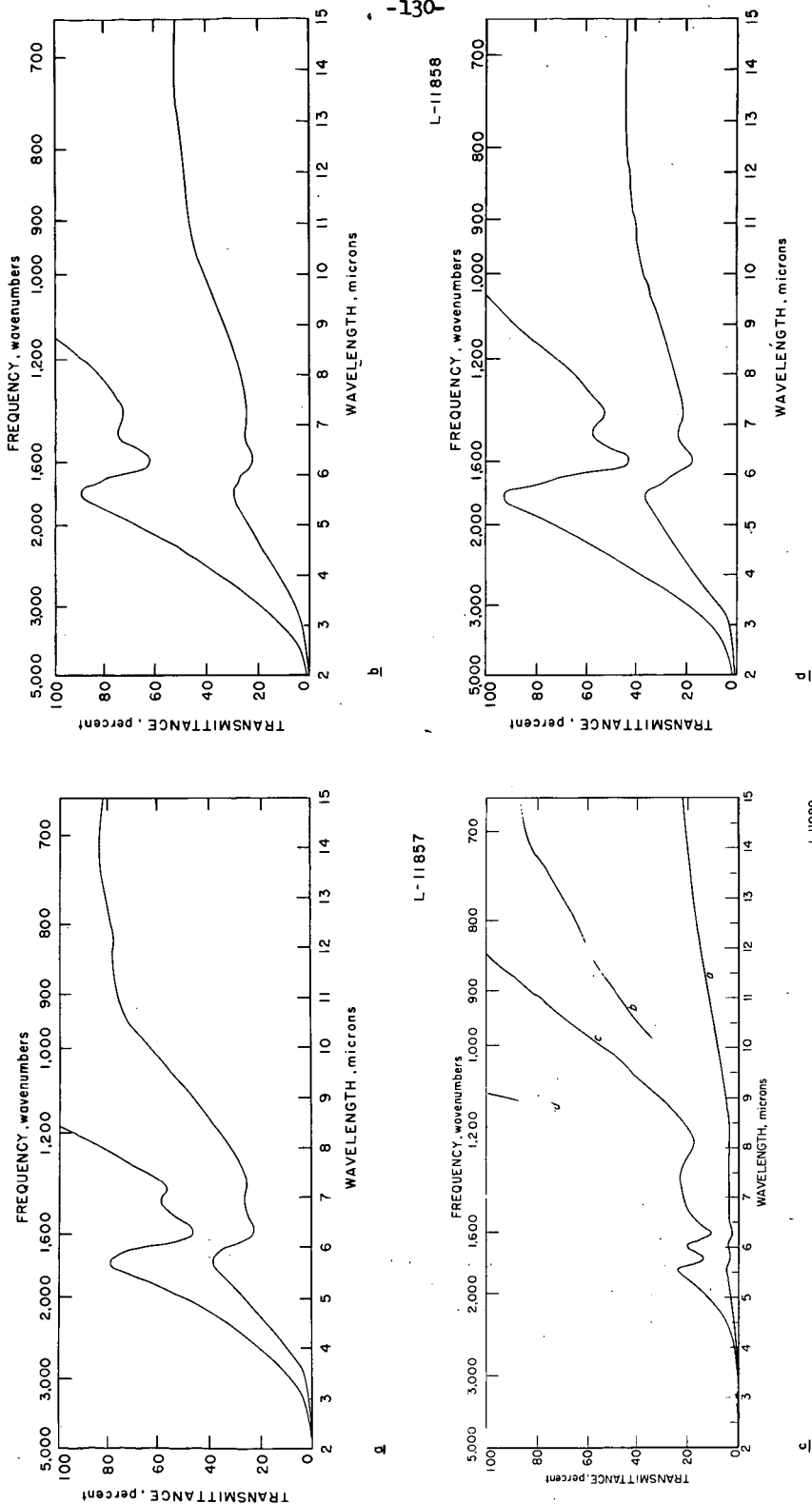


Figure 4. Infrared spectra: (a) Channel black; (b) carbon black from coal; (c) activated carbon from coal (CAL carbon); (d) activated carbon from cocconut (UCC carbon). In each case the top curve(s) are scale-expanded.

Table 3.- Raman spectra of coals, graphite, and carbons (in cm⁻¹)

Coals

Lignite (74.2% C) Baukol-Noonan Strip Mine Noonan Bed, Divide Co., N. Dak.	1600 (s,br) ^{a/}	1350 (w,br)	1200 (w)	705 (w)
Subbituminous (78.7% C) Rock Springs No. 7 Bed, Clark Mine Sweetwater Co., Wyo.	1620 (s,br)	1380 (br)		720 (w)
hvbB (80.5% C) No. 6 Bed, Atkinson Mine, Hopkins Co., Ky.	1605 (s)	1390 (m)		
hvaB (82.4% C) Pittsburgh No. 8 Bed, Piney Fork No. 1 Mine, Jefferson Co., Ohio	1610 (m)	1380 (m)		
hvaB (83.1% C) Pittsburgh Bed, Bruceton Mine, Allegheny Co., Pa.	1607 (s)	1382 (m)		
lvb (90.0% C) Pocahontas No. 3 Bed, Buckeye No. 3 Mine, Wyoming Co., W. Va.	1609 (s)	1355 (s)		
Anthracite (94.2% C) St. Nicholas Breaker, Reading Coal Co., Reading, Pa.	2960 (s,br)	1610 (s,shp)	1340 (m)	1200 (br)

Table 3.- Raman spectra of coals, graphite, and carbons (in cm^{-1})
(cont'd)

<u>Graphites and Carbons</u>	
Graphite, pyrolytic, highly oriented (UCC)	1582 (s,shp)
Graphite powder (UC)	1580 (w) (very w)*
CAL activated carbon	1600 (m) 1340 (m)
Channel black (Micronex)	1600 (s) 1340 (w) 1180 (m)
Graphite, single crystal ^{b/}	1575 (s,shp)
Graphite, polycrystalline ^{b/}	1575-1592 (s,shp) 1355 (m)
Activated charcoal ^{b/}	1575 (m) 1355 (m)

a/ s = strong; m = moderate; w = weak; br = broad; shp = sharp;
h = high; l = low; v = volatile; b = bituminous; A, B = classifications of hvb coals.
b/ Reference 14.
* A very weak line may be present at about 1360 cm^{-1} .

on this broad band system in coal spectra are CH bands at 1460 and 1375 cm^{-1} and broad absorption usually attributed to phenolic structures at 1250 cm^{-1} . The absorption due to phenoxy groups at 1250 cm^{-1} , presumably phenols, is probably very weak, and the major absorption is likely due to the graphitic structure. The overall structure of this wide band system, 1800-900 cm^{-1} , has always been a mystery. The broad, intense infrared band at $\sim 1360 \text{ cm}^{-1}$ has been attributed completely to the obvious bands at 1460, 1375, and 1250 cm^{-1} . The broad structure centering on 1250 cm^{-1} has usually in the past been assigned to phenolic structures, but this assignment never made particular sense because there are not tremendous concentrations of phenols in coals. It makes more sense to assign a small amount of this 1800-900 cm^{-1} absorption to phenolic and CH structures and the major portion of the absorption to the graphitic structures.

In studies of infrared spectra of coals an anomaly involving the intensities of aliphatic CH stretching and bending frequencies has remained unsolved until now. The aliphatic CH stretching frequency in spectra of organic substances nearly always produces a more intense band than the CH bending frequencies; in coal spectra, however, the intensities are reversed. We can now see that the bending frequencies have greater apparent intensity because of intense broad absorption produced in this spectral region by "graphitic" components.

Specifically, we are assigning the 1800-900 cm^{-1} absorption mainly to graphitic structures. Aromatics cannot be excluded, and small amounts are known to be present, but these cannot account for the broad 1800-900 cm^{-1} absorption nearly as well as highly absorbing graphitic structures.

Aliphatic structures such as quaternary carbon atoms in diamond-type structures need to be considered. The presence in coals and carbons of diamond-like structures was proposed in 1959.²⁴ The presence or absence of such structures has remained debatable; the new spectral data presented herein provide some information on this point. The infrared measurements on diamonds indicate that two kinds of spectra exist: (1) Type I diamonds have infrared absorption in two spectral regions, 4000 to 1800 cm^{-1} and 1400 to 1000 cm^{-1} ; (2) Type II diamonds have only the one absorption region, 4000 to 1800 cm^{-1} ; it is significant that Type II diamonds have essentially no absorption at frequencies from 1800 to at least 400 cm^{-1} .²⁵ Type II diamonds are in fact used as transparent cell windows for special infrared cells. The most intense absorption band observed for diamonds, 1290 cm^{-1} , has a very small absorption coefficient, 0.0039 liter/gm cm. The corresponding coefficient for the 1600 cm^{-1} band in coal spectra is 0.49 liter/gm cm. Thus, if the carbon atoms of coal were all in diamond structures, these structures could account for no more than $.0039/.49 \times 100$ or 0.8 percent of the observed absorption. The remaining absorption, 99.2 percent, would have to come from some other source. This evidence supports our assignment of the intense absorption in the spectra of coals and carbons at 1600 and 1360 cm^{-1} to strongly absorbing graphitic structures.

By this assignment spectroscopists have nearly gone full circle in two decades from assigning the 1600 cm^{-1} band to aromatic structures, then to conjugated chelated carbonyls, and lastly, to a graphitic structure. The assignment of the long unknown source of the absorption from 1800 to 900 cm^{-1} is very important. This spectral region was the principal remaining unknown absorption in coal spectra. The presence of a graphitic type, non-crystalline structure is a most important contribution to the study of coal structure. Graphitic structures will almost certainly remain behind after thermal reactions liberate volatile materials; it is obvious that graphitic structures, crystalline or amorphous, will not be volatile nor extractable.

It is quite possible that the components emitted from coal under coking conditions or other thermal conditions may be materials that were trapped in the molecular sieve structure of coal. Anderson at the U.S. Bureau of Mines first demonstrated that coals are molecular sieves.^{26/} Vahrman has recently stated that from his work on exhaustive extraction he believes the extractable organic components of coals are released from molecular sieve structures.^{27/} Molecular sieve structures may constitute the residues that remain behind after extraction or carbonization. Apparently no studies have been made on carbonaceous residues to ascertain whether or not they also possess properties of molecular sieves.

SUMMARY

Infrared and Raman spectra of the intractable carbonaceous materials are difficult to obtain. For coals, carbon blacks, and chars prepared at low temperatures infrared spectra have been obtained with relative ease. Activated carbons are difficult to grind down to small particle sizes, and only recently have good infrared transmission spectra been obtained. More difficult materials have now been successfully studied by the transmission infrared method--most notably ground graphite, high-temperature carbons, high-temperature chars, and carborundum. After long grinding graphite loses its crystallinity but the molecular structure of the carbon matrix apparently remains unchanged; broad, intense infrared bands are observed at about 1590 and 1360 cm^{-1} for ground graphite and for some activated carbons.

The frequencies of the two broad infrared bands are in excellent agreement with the frequencies of the two laser-Raman lines found for various carbons: ~1600 and 1360 cm^{-1} . The laser-Raman spectra are the same for coals, carbons, and graphites. However, the similarity of these laser-Raman spectra indicate in the case of coal that we may be observing the spectrum of carbonized coal rather than of coal. Coal may burn or carbonize in the laser beam.

In the light of these new spectral results, reassignment of some bands in the infrared spectra of coals has become necessary. Graphite-like structures (non-crystalline) are believed to be responsible for the broad 1600 cm^{-1} band in coals, and the broader 1360 cm^{-1} band, which appear to fit closely the broad band contour from 1800 to 900 cm^{-1} in the infrared spectra of coals. The intensities of the 1600 and 1360 cm^{-1} bands in ground graphite are more than sufficient to account for the band intensities observed in the spectra of coals and chars. Diamond-like structures such as quaternary carbon atoms do not appear to be involved.

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